

Using Accelerated Tests to Predict Service Life of Organic Materials Subjected to Outdoor Weathering

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Abstract

Today's manufacturers need accelerated test (AT) methods that can usefully predict service life in a timely manner. For example, automobile manufacturers would like to develop a 3-month test to predict 10-year field reliability of a coating system (an acceleration factor of 40). Developing a methodology to simulate outdoor weathering is a particularly challenging task and most previous attempts to establish an adequate correlation between laboratory tests and field experience has met with failure. Difficulties arise, for example, because the intensity and the frequency spectrum of ultraviolet (UV) radiation from the Sun are highly variable, both temporally and spatially and because there is often little understanding of how environmental variables affect chemical degradation processes.

This paper describes the statistical aspects of a cooperative project being conducted at the US National Institute of Standards and Technology (NIST) to generate necessary experimental data and the development of a model relating cumulative damage to environmental variables like UV spectrum and intensity, as well as temperature and relative humidity. The parameters of the cumulative damage model can be estimated from laboratory data. The model will be verified by comparing with specimens tested in an outdoor environment for which the environmental variables were carefully measured. Then predictions for future service life can be made as a function of a stochastic process model that characterizes environmental variables (e.g. weather) in a given location. Using a spatial-temporal model for weather, one can make predictions for a product population.

1 Introduction

Photodegradation, caused by UV radiation, is a primary cause of failure for paints and coatings (as well as other organic materials) exposed to sunlight. Other variables that affect degradation rates include temperature and humidity. Manufacturers of such paints and coatings have had difficulty in using laboratory tests to predict field experience with their products. Most of the laboratory tests attempt to accelerate time by "speeding up the clock." This is done by increasing average level of experimental factors like UV radiation, temperature, and humidity and cycling these experimental factors more rapidly than what is seen in actual use, in an attempt to simulate and accelerate outdoor aging. Such experiments violate some of the rules of good experimental design (e.g., by varying important factors together in a manner that confounds the effects of the factors) and the high levels of the accelerating variables can induce new failure modes. Thus such accelerated tests provide little fundamental understanding of the underlying degradation mechanisms. Because experience has shown that the results of these tests are unreliable, standard product evaluation for paints and coatings still requires outdoor testing in places like Florida and Arizona (hot humid and hot dry environments, respectively). Such testing, however, is costly and takes too much time.

Martin, Saunders, Floyd, and Wineburg (1996) and Martin (1999) provide a detailed description of issues relating to prediction of service life for paints and coatings. In general the accelerated test methodology for photodegradation is much more complicated than those typically used for electronic and mechanical devices (e.g., as described in Nelson 1990 and Chapters 18-21 Meeker and Escobar 1998). This is because of the complicated chemical/physical failure mechanism involved and the highly-variable use environment.

2 A General Approach to Service Life Prediction in Complicated Environments

As described above, tests that simply “speed up the clock” have not provided consistently adequate predictions of field performance of organic paints and coatings. In general, the mechanistic modeling of failure mechanisms and their dependency on accelerating variables is important for the successful application of accelerated testing. Statistical characterization of the product=use environment is also important. In order to do realistic service life prediction for complicated environments based on accelerated laboratory tests, we propose the following general approach, generalizing the traditional methods described in the previous section.

1. Use understanding of the physical/chemical mechanisms underlying product degradation and failure along with the experimental results to develop a deterministic product degradation model. To be workable, it will be necessary to develop a relatively simple model that, for example, identifies and focuses on the rate-limiting steps in the overall failure model.
2. Conduct laboratory experiments, using standard principles of experimental design, to gain fundamental understanding of the mechanisms leading to failure. Factors studied in the experiment should correspond to the environmental variables that affect service life. The experimental effort should lead to a model that will predict degradation rate as a function of the experimental/environmental variables.
3. Use environmental time series data on the important factors that affect degradation (e.g., UV radiation, temperature, humidity) to characterize the environment. This could be done, for example, by identifying multivariate time series models for particular locations of interest.
4. Use the model for environmental variability in Step 3. along with the physical/chemical mechanism model identified in Step 1. to define a predictive stochastic process model for product degradation in the field.
5. Compare the results from outdoor testing (where the environmental variables are carefully monitored) with model predictions from the service life prediction model.

3 Time Scale for Photodegradation

It is well known that it is important to choose an appropriate time scale to describe the behavior of a failure mechanism (e.g., number of miles for an automobile engine bearing or number of cycles for fatigue caused by cyclic stress). This section describes the appropriate time scale for photodegradation. Many of the ideas in this section originated from early research into the effects of light on photographic emulsions (e.g., James 1977) and the effect that UV exposure has on causing skin cancer (e.g., Blum 1959).

3.1 Model for total effective UV dosage

As described in Martin et al. (1996), the appropriate time scale for photodegradation is D_{Tot} , the total effective UV dosage. Intuitively, this total effective dosage can be thought of as the number of photons absorbed into the degrading material. The total effective UV dosage at real time t can be computed from

$$D_{\text{Tot}}(t) = \int_0^t D_{\text{Inst}}(t) dt$$

where the instantaneous effective UV dosage D_{Inst} is

$$D_{\text{Inst}}(t) = \int_{\lambda_1}^{\lambda_2} E_0(\lambda, t) \{1 - \exp[-A(\lambda)]\} \phi(\lambda) d\lambda. \quad (1)$$

Here is E_0 the spectral irradiance of the light source (both artificial and natural light sources have mixtures of light at different wave lengths), $[1 - \exp(-A(\lambda))]$ is the spectral absorbance of the material being exposed

(damage is caused only by photons that are absorbed into the material), and ϕ is the quantum efficiency of the absorbed radiation (allowing for the fact that photons at certain wavelengths have a higher probability of causing damage than others). All of the functions in the integrand of (1) can either be measured directly (E_0) or estimated from experimental data (A and ϕ). The integral in (1) is typically taken over the UV-B band (290-320 nm), as this is the range of wavelengths over which both $\phi(\lambda)$ and $E_0(\lambda, t)$ are importantly different from 0. Larger wavelengths (in the UV-A band) are not harmful ($\phi(\lambda) \approx 0$). Lower wavelengths (in the UV-C band) have more energy, but are filtered by ozone in the atmosphere ($E_0(\lambda, t) \approx 0$).

3.2 Reciprocity and reciprocity breakdown

The intuitive idea behind reciprocity in photodegradation is that the time to reach a certain level of degradation is inversely proportional to rate at which photons attack the material being degraded. Reciprocity breakdown occurs when the coefficient of proportionality changes with light intensity.

Although reciprocity provides an adequate model for some degradation processes (particularly when the range of intensities used in experimentation and actual applications is not too broad) numerous examples have been reported in which there is reciprocity breakdown (e.g., Blum 1959 and James 1977). Light intensity can be affected by filters. Sunlight is filtered by the earth's atmosphere. In laboratory experiments, neutral density filters are used reduce the amount of light passing to specimens (without having an important effect on the wavelength spectra), providing an assessment of the degree of reciprocity breakdown.

Reciprocity also implies that the effective time of exposure is

$$d(t) = CF \times D_{\text{Tot}}(t) \quad (2)$$

where CF is a “celeration factor.” For example, commercial outdoor test exposure sites use mirrors to achieve, say “5 Suns” *acceleration* or $CF = 5$. A 50% neutral density filter in a laboratory experiment will provide *deceleration* corresponding to $CF = 0.5$.

When there is evidence of reciprocity breakdown, the effective time of exposure is often modeled by

$$d(t) = (CF)^p \times D_{\text{Tot}}(t). \quad (3)$$

This model has been shown to fit data well and experimental work in the photographic literature suggests that when there is reciprocity breakdown, the value of p does not depend on wavelength λ . A statistical test of $p = 1$ can be used to assess the reciprocity assumption.

4 Model for Photodegradation

4.1 Degradation response model

Degradation at time t , $\mathcal{D}(t)$, usually depends on environmental variables like E_0 , **temp**, and **RH**, that vary *over time*, say according to a multivariable profile $\xi(t) = [E_0, \text{temp}, \text{RH}, \dots]$. Laboratory tests are conducted in well-controlled environments, usually holding these variables constant (although sometimes such variables are purposely changed during an experiment, as in step-stress accelerated tests). Interest often centers, however, on life in a variable environment.

The degradation responses being used in the NIST experiments are specific peaks in measured FTIR spectra. The heights of the peaks correspond to the amount of particular chemical products. Through the range of interest (that is up to the point where $\mathcal{D}(t)$ has reached a failure state) we have found, empirically, that the functional form

$$\begin{aligned} \mathcal{D}(t) &= \mathcal{D}(0) + [\mathcal{D}(\infty) - \mathcal{D}(0)] \left[\frac{\exp(z)}{1 + \exp(z)} \right] \\ z &= \frac{\log[d(t)] - \mu}{\sigma}. \end{aligned} \quad (4)$$

fits the data well for all FTIR peaks of interest and at all combinations of the experimental factors. Here from (3), $d(t) = (CF)^p \times D_{\text{Tot}}(t)$ is the effective dosage, corrected for reciprocity breakdown. Also, $\mathcal{D}(0)$ is

the observed level of degradation at time 0 and $\mathcal{D}(\infty)$, μ , and σ are unknown parameters that are estimated from the data.

To provide a model for the effects of temperature and humidity, as well as intensity, we expect to use the extended model

$$\begin{aligned}\log(d; \text{CF}, p) &= \log[\mathcal{D}_{\text{Tot}}(t)] + p \times \log(\text{CF}) \\ \mu &= \beta_0 + \frac{E_a}{k_B \times \text{temp K}} + C \times g(\text{RH})\end{aligned}\tag{5}$$

where temp K is temperature Kelvin, $g(\text{RH})$ is a model prediction of moisture content, as a function of relative humidity (all of the environmental variables are potentially functions of time), k_B is Boltzmann's constant, E_a , an effective activation energy, β_0 , and C are parameters that are characteristic of the material and the degradation process.

4.2 Total degradation in a time-varying environment

For some applications, it will be necessary to evaluate \mathcal{D} as a function of time, under a nonconstant environment. Let $d\mathcal{D}[\tau; \boldsymbol{\xi}(\tau)]/d\tau$ be the degradation rate at time τ where $\boldsymbol{\xi}(\tau)$ is the vector of environmental conditions at that time.

For a given environmental profile $\boldsymbol{\xi}(t)$, the cumulative degradation at time t for a particular unit) can be expressed as

$$\mathcal{D}(t; \boldsymbol{\xi}) = \int_0^t \frac{d\mathcal{D}[\tau; \mathcal{D}_{\text{Inst}}(\tau), \text{temp}(\tau), \text{RH}(\tau), \dots]}{d\tau} d\tau\tag{6}$$

where $d\mathcal{D}[\tau; \boldsymbol{\xi}(\tau)]/d\tau$ is the degradation rate and $\boldsymbol{\xi}(\tau)$ is the vector of environmental conditions at time τ . The integral is reasonably easy to compute after appropriate discretization of the time axis.

4.3 Stochastic degradation model

The environmental variables in $\boldsymbol{\xi}(t)$ are controlled in laboratory tests, but will be stochastic over time in actual product use. In order to evaluate the distribution of degradation paths for a stochastic environment, one can still use (6), but the integral becomes a stochastic integral. One straightforward, but computationally intensive method of evaluating (6) is simulate $\boldsymbol{\xi}(t)$ paths from a multivariate time series model for the environment and use these to obtain simulated \mathcal{D} paths.

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